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## ISOLATION OF BORON AND CARBON ATOMS IN CRYOGENIC SOLIDS

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### ABSTRACT

Boron and carbon atoms, and their dimmers and trimers were isolated in solid argon by co-condensation of their vapors onto a substrate maintained at 10 K. Growth and disappearance of various clusters with 3 to 12 atoms that occurred during annealing was studied by quantitative Fourier Transform Infrared Spectroscopy. The annealing experiments indicated that the initially formed solids contained about 80 % B and C atoms and BC molecules. At 5 mole percent atom concentration these High Energy Density Materials (HEDM) could be applied in propulsion where they are capable of producing about 25% higher specific impulse than the best rocket engines fueled by liquid hydrogen and liquid oxygen.

### INTRODUCTION

Production of a cryogenic matrix with an atom density of  $\sim 1 \times 10^{21}$  atoms  $\text{cm}^{-3}$ , which amounts to  $\sim 5$  mole percent atoms in an inert solid, or an equivalent atom gas pressure of  $\sim 60$  atm at 298 K, has been pursued under the auspices of the U. S. Air Force High Energy Density Matter (HEDM) Program [1]. Isolation of boron atoms in solid para hydrogen at  $\sim 4$  K would produce a cryogenic solid propellant capable of providing around 25% larger specific impulse than that available from the best rocket engines fueled by liquid hydrogen and liquid oxygen. Thus, studies over the past decade have focused on production of matrices doped with lightweight atoms. To determine the fractional mass of dopant isolated as atoms, it is necessary to identify and measure the small clusters that inevitably must form upon warming of the matrix. Tam and Fajardo [2], using laser ablation of solid boron and uv/vis spectroscopy, isolated B atoms in rare gas and para-hydrogen solids at 4 K; they also identified  $\text{B}_2$  in rare gas but not para hydrogen solids. *Ab-initio* calculations have shown [3] that B atoms have a 12 kcal/mol barrier for reaction with  $\text{H}_2$ , but C atoms have no barrier [4] and could therefore never be isolated in solid hydrogen.

Currently, the Air Force Office of Scientific Research is supporting basic research on characterization of the states of aggregation of boron in cryogenic solids through the International Research Initiative administered by the European Office of Aerospace Research and Development, London. One product of this support, the first optical spectrum of the  $\text{B}_3$  molecule, was recently reported and analyzed in detail [5]. This is an important contribution toward understanding boron HEDM because  $\text{B}_3$  is a cyclic molecule so it probably resists attack by other atoms and radicals at low temperatures.  $\text{B}_3$  is thought to be an "island of stability" beyond which further condensation could not occur in boron HEDM. Recent *ab-initio* studies and calculation of rate constants by RRKM theory [6,7] indicate that boron atoms, once isolated, would be stable in solid hydrogen.

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Key Word: High Energy Density Matter, HEDM, Boron Vapor, Boron Cluster, Matrix Isolation Spectroscopy

One of the greatest experimental difficulties with boron is caused by the extreme corrosiveness of liquid boron, which is a universal solvent. Under the auspices of the Small Business Innovative Research Program, the Air Force Research Laboratory recently developed a robust, high-flux boron vapor source for rapid preparation of  $\sim 100$  mg samples of 5-mole percent B vapor in cryosolids in  $\sim 2$  hours [8]. Here, a boron sphere inside a vacuum chamber is heated to melting by absorption of a beam of IR energy from an external cw CO<sub>2</sub> laser. A pool of liquid develops that is contained by solid. The vaporization process is self-regulated because the liquid surface reflects the laser energy, and vaporization occurs from the liquid at its melting point (2360 K) at a well-controlled flux. The cryosolid is produced in the usual way by co-condensation with rare gas or para hydrogen onto a substrate maintained at  $\sim 4$  K.

## BACKGROUND

The first experimental evidence of B<sub>j</sub>C<sub>n-j</sub> was reported 35-years ago by Verhaegen, Stafford, and Drowart [12]. They used mass spectrometry to study boron and boron carbide vaporization from graphite Knudsen cells that were heated by electron bombardment to temperatures up to 2500 K. The measured vapor pressure of boron at 2200 K was  $\sim 0.008$  torr, 94% atoms, 5% BC<sub>2</sub>, 1% B<sub>2</sub>C, and 0.07% BC. At the same temperature, boron carbide had about one-half the vapor pressure with 96% atoms, 4% BC<sub>2</sub>, 0.1% B<sub>2</sub>C. Distributions of anions and cations of B<sub>x</sub>C<sub>y</sub> with up to 17-atoms have been measured in plumes of laser vaporized boron carbide targets by Becker and Dietze [13]. Their mass spectrometric analysis showed that B<sub>2</sub>C<sup>-</sup>, B<sub>2</sub>C<sup>+</sup>, BC<sub>2</sub><sup>-</sup>, and BC<sub>2</sub><sup>+</sup> were major components of the plume. Matrix isolated BC<sub>2</sub> has been produced by oven and laser vaporization of carbon/boron mixtures and targets and measured by FTIR [9, 14] and ESR [15, 16] spectroscopy. More recently, Wyss, Grutter and Maier [17] isolated BC<sub>2</sub><sup>-</sup> and BC<sup>-</sup> in neon matrices by sputtering a boron carbide target with Cs<sup>+</sup> and trapping the mass-selected anions in neon matrices. Neutrals were produced by electron photo-detachment with uv radiation. Electronic transitions of BC<sub>2</sub> and BC and their anions were studied. The FTIR spectrum of the previously identified [9]  $\nu_2(a_1)$  fundamental of BC<sub>2</sub> was also observed. The infrared spectrum of BC has never been measured, but a CCSD(T)/cc-pVTZ calculation with quartic force field predicted [18] its vibrational fundamental at 1148 cm<sup>-1</sup> with intensity of 43 km mol<sup>-1</sup>. Of the pure boron clusters, only B<sub>3</sub> has been experimentally observed. Li, Van Zee and Weltner [19] identified all four isotopomers of B<sub>3</sub> in argon matrices by FTIR spectroscopy and found that experimental frequencies matched *ab-initio* frequencies of its cyclic geometry. Although *ab-initio* studies of B<sub>n</sub>,  $n > 4$ , have been carried out, only geometries and energies have been reported [20, 21]. Unlike C<sub>n</sub>, B<sub>n</sub> for  $n > 4$  are predicted to have stable 3-dimensional geometries.

Carbon clusters were recently reviewed by Van Orden and Saykally [22]. Cyclic C<sub>6</sub> [23, 24], cyclic C<sub>8</sub> [25, 26], linear C<sub>11</sub> [27], have recently been identified by FTIR spectroscopy of clusters isolated in solid argon. Most recently, electronic spectra linear C<sub>17</sub>, C<sub>19</sub>, and C<sub>21</sub> [28] and cyclic C<sub>10</sub> and cyclic C<sub>12</sub> [29] isolated in neon matrices were reported, and Raman spectra of linear C<sub>16</sub>, C<sub>18</sub>, and C<sub>20</sub> were reported [30].

In this paper, qualitative and quantitative analysis of B<sub>j</sub>C<sub>n-j</sub> clusters in prototypical HEDM is presented up to clusters with  $J = 9$ . Previously, the first conclusive identifications of small boron clusters, BC<sub>2</sub>, B<sub>2</sub>C, BC<sub>3</sub>, and B<sub>2</sub>C<sub>2</sub>, were reported [9-11] where observed FTIR fundamentals and isotope shifts were matched with predictions of *ab-initio* theory.

## EXPERIMENTAL

Mixtures of boron and carbon powders were evaporated with a resistively heated oven to temperatures  $\sim 3000$  K, and vapors were co-condensed with  $\sim 1000:1$  excess argon at 10 K to form  $\sim 60$  micrometers thick matrices in about one-hour. A precision matched pair of matrices was prepared as described in Ref. [9] with two different boron isotopic compositions and natural abundance carbon. Matrix (a) contained natural abundance boron,  $^{11}\text{B}/^{10}\text{B} = 4.0$ , and matrix (b) contained boron with an inverted isotope ratio,  $^{11}\text{B}/^{10}\text{B} = 0.37$ .

Each matrix had a [C/B] molar ratio of  $\sim 3.0$ , a thickness of  $\sim 60 \mu\text{m}$ , and very similar absolute amounts of each element. Each matrix was annealed repeatedly to temperatures between 25 K and 40 K and spectra were recorded after each annealing as described in more detail below.

## RESULTS AND DISCUSSION

Fig. 1 shows a Pascal's triangle representation of the boron/carbon cluster system. In the limit of statistical recombination of well mixed atoms, the relative yields of  $B_J C_{n-J}$  clusters of given  $n$  is given by

$$\rho(B_J C_{n-J}) / \rho(C_n) = n! / J!(n-J)! [B/C]^J, \quad (1)$$

where  $[B/C]$  is the molar ratio of boron to carbon, and  $\rho(i)$  is the column density of species  $i$ .

Beer's Law enables quantitative analysis of the various species,  $\rho_i = 2.303 A_i(\text{experiment}) / I_i(\text{theory})$ , where  $\rho_i$  is the average column density of species  $i$ , which is the average value of the product of the species density and matrix thickness.  $A_i(\text{experiment})$  is the measured integrated intensity of the infrared absorbance of species  $i$ .  $I_i(\text{theory})$  is the infrared absorption intensity of species  $i$ , which by necessity must be obtained by theoretical ab-initio calculation because experimental values are not available at this time. Fig. 1 indicates values of  $I_i(\text{theory})$  for various clusters that were obtained by DFT/cc-pVDZ [31-34].

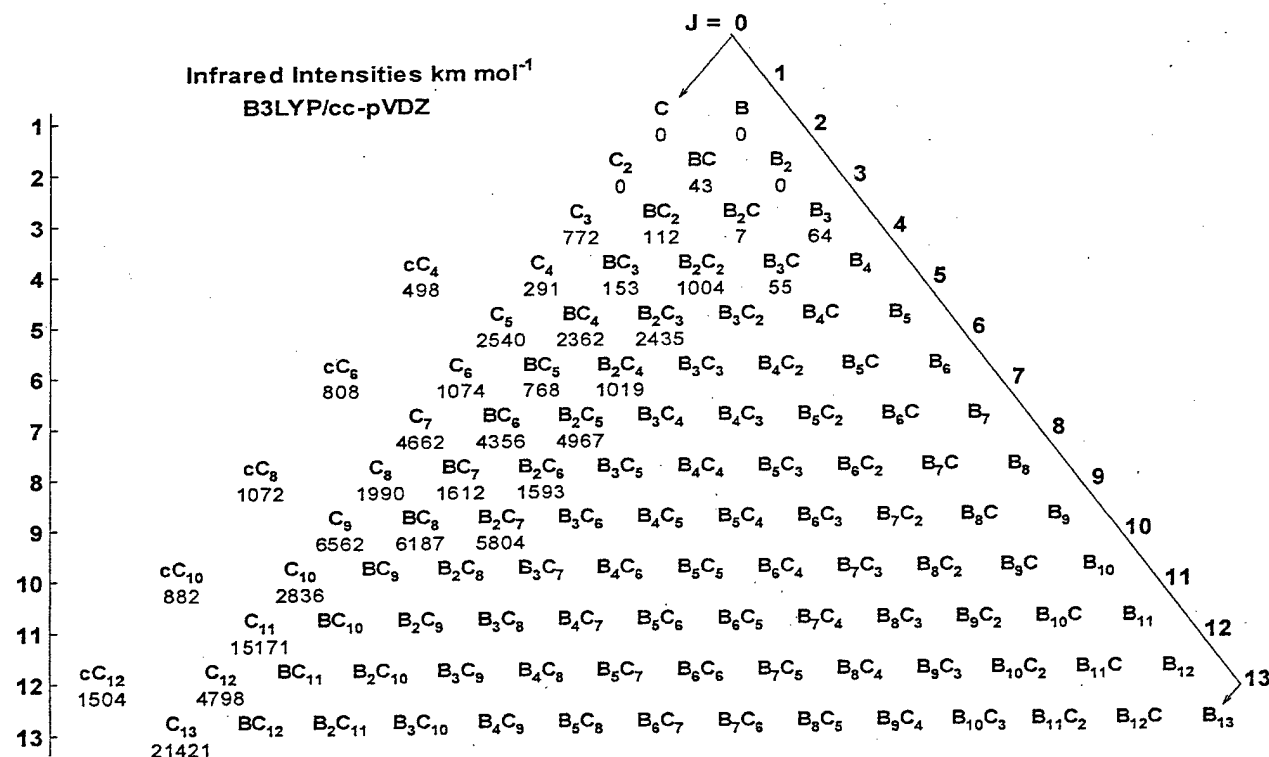


Figure 1. Representation of the  $B_J C_{n-J}$  ( $n = 1 - 13$ ,  $J = 0 - n$ ) system by Pascal's triangle. Numbers below molecular formulas denote the ab-initio intensities of the most intense infrared stretching fundamentals, Refs. [31] - [34]. Cyclic carbon clusters are removed from the triangle to the left.

Fig. 2 shows a survey spectrum of an annealed matrix with  $C/B \sim 3$ . Quasi-linear  $C_3$  and cyclic  $BC_2$ ,  $B_2C$ , and  $B_3$ , constituted about 80% of the total observable boron and carbon in the initially deposited matrix. Approximately statistical distributions [Eq. 1] among the  $J = 0, 1$ , and 2 clusters were measured in clusters with  $n = 3, 4$ , and 5 as discussed in greater detail below.

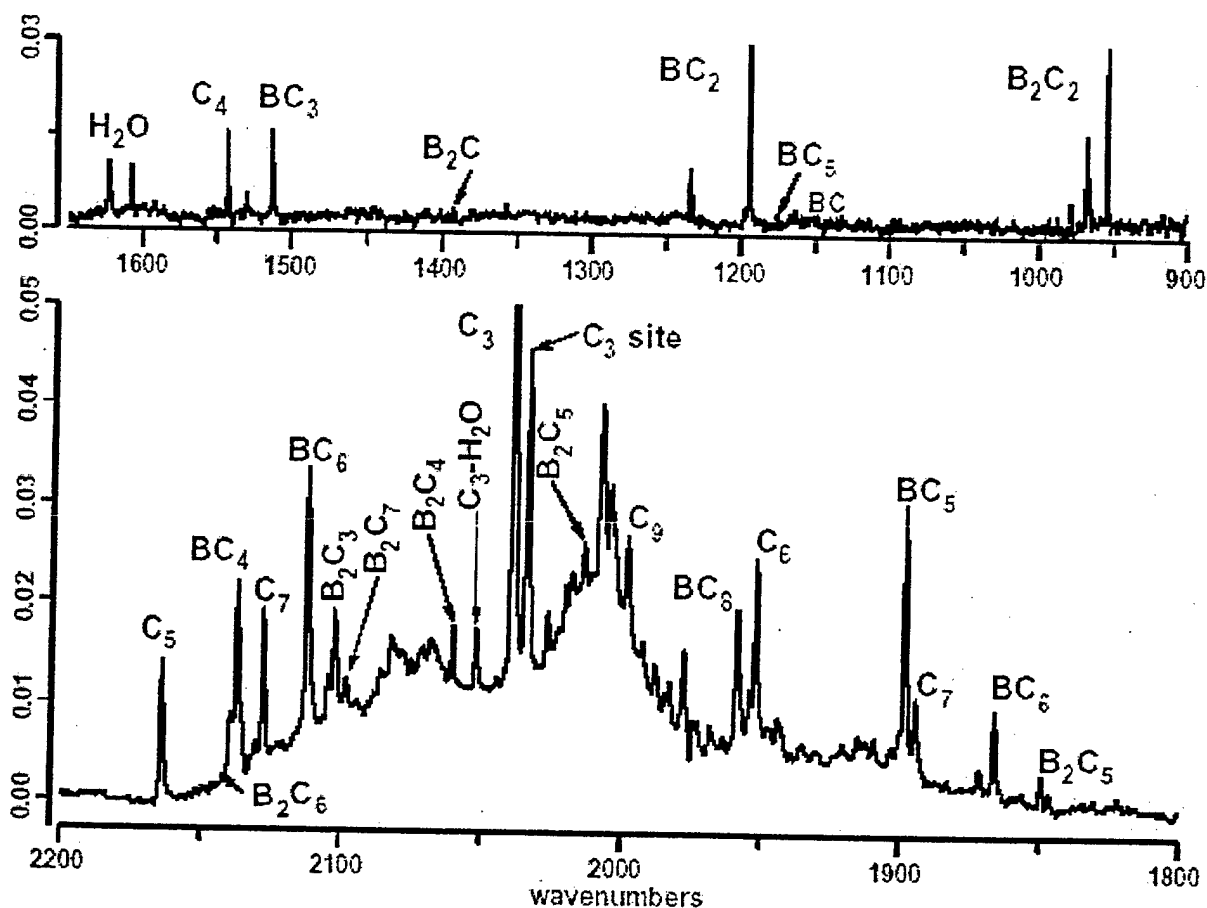


Figure 2. Survey spectrum of matrix containing carbon and boron clusters at natural isotopic abundance with  $[B/C] \sim 1/3$  after three annealings. Fundamentals of  $BC_{n-1}$  for  $n = 4, 5, 6, 7$ , and  $9$  are similarly red-shifted from fundamentals of linear  $C_n$ , and their experimental absorbances are all slightly greater in this matrix. Two fundamentals of  $BC_6$  are observed at  $2112$  and  $1866$   $cm^{-1}$ , redshifted from the two fundamentals of linear  $C_7$ .

Figure 3 shows the annealing behaviors of the FTIR bands belonging to  $BC_2$ ,  $BC_3$  and  $B_2C_2$  for each of the two precision matched matrices.  $BC_2$  disappears entirely due to reaction at one of its carbon atoms with a radical species, which results in opening of the  $BC_2$  ring. The dramatic appearance of  $B_2C_2$  during the first annealing is consistent with a mechanism involving recombination of  $BC$ , whose density lies below the limit of detection, or condensation of  $B$  atoms with  $BC_2$ .

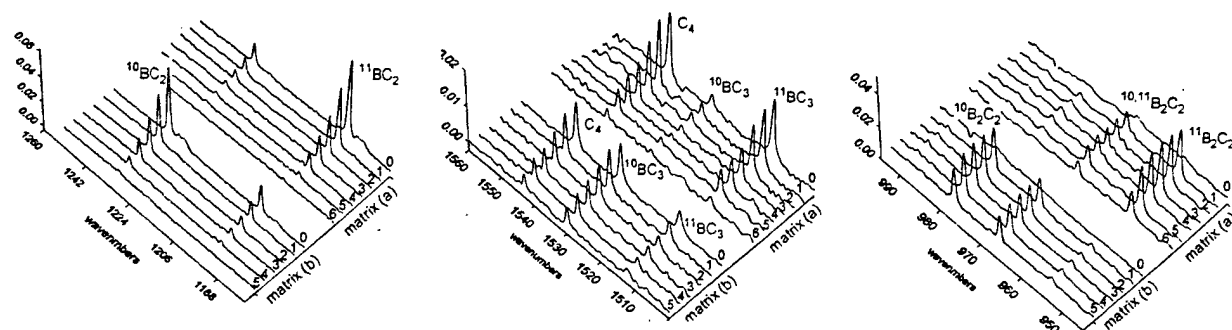


Figure 3. Absorbance spectra of matrix (a) and matrix (b) showing disappearance of  $BC_2$ ,  $BC_3$  and  $C_4$ , and appearance of  $B_2C_2$  upon annealing. Spectra labeled "0" are spectra of originally deposited matrices. Annealing temperatures and times were (1)  $27.5$  K/ $150$  s, (2)  $30.0$  K/ $75$  s, (3)  $32.5$  K/ $45$  s, (4)  $35.0$  K/ $30$  s, (5)  $37.5$  K/ $20$  s, (6)  $40.0$  K/ $20$  s. The decrease in the peaks in the fifth and sixth annealing is due to matrix sublimation. The red-shift of the  $BC_3$  absorption from the  $C_4$  absorption is indicative of red shifts observed for all the other  $BC_{n-1}$  clusters when a boron atom is substituted for a carbon atom in a  $C_n$  cluster.

Fig. 4 shows the annealing behaviors of the  $^{11}\text{B}_J^{12}\text{C}_{n-1}$  clusters,  $n = 3$  to  $9$  and  $J = 0, 1, 2$  that were measured in matrix (a). Loss of clusters during the sixth annealing by matrix sublimation is generally greatest for  $\text{C}_n$

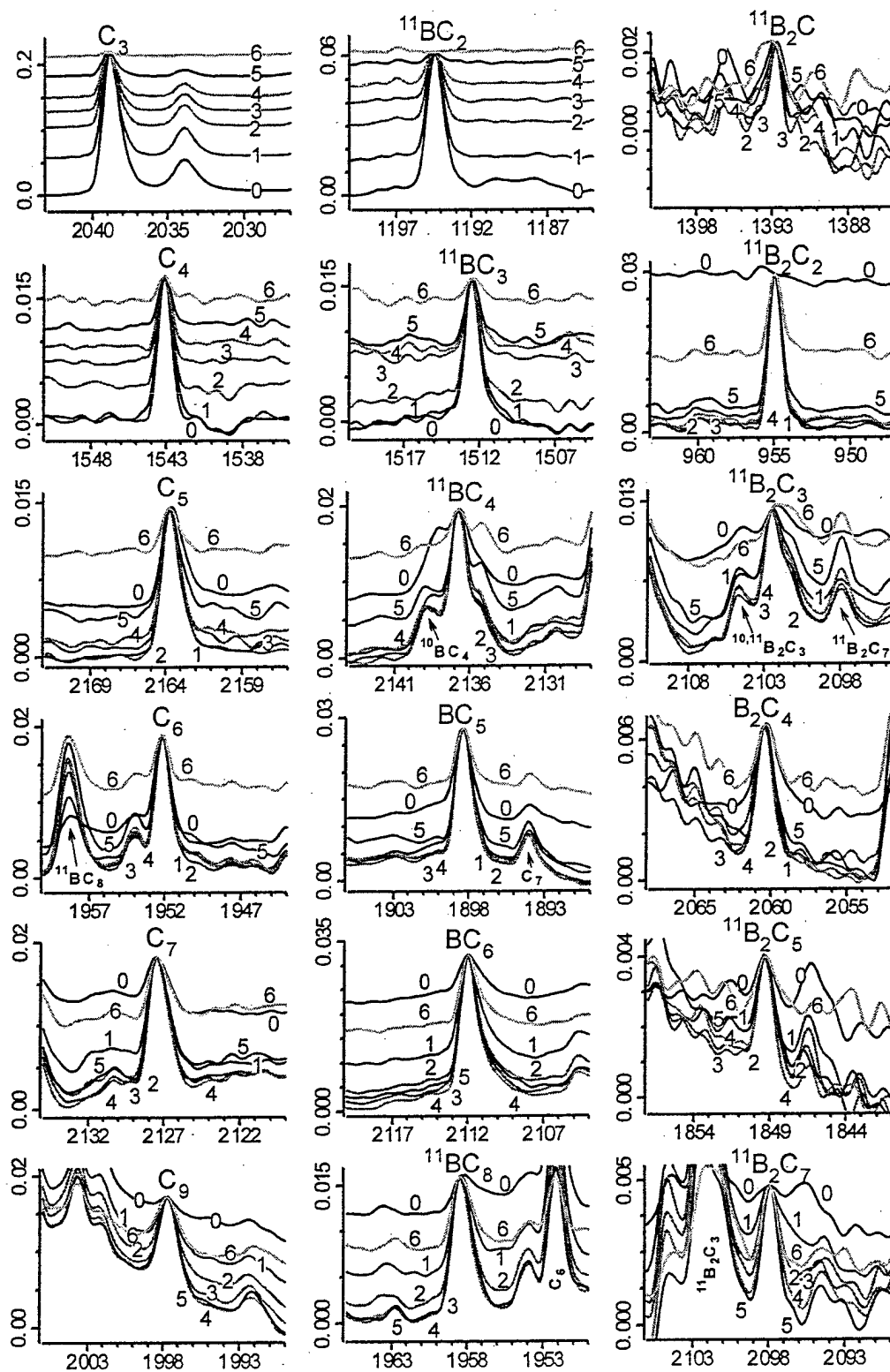


Figure 4. Annealing behaviors of  $\text{B}_J\text{C}_{n-J}$  species in matrix (a). Spectra labeled '0' were obtained from the originally deposited matrix, and spectra labeled '1' to '6' were obtained after successive annealings as detailed in the Fig. 3 caption. Absolute absorbance scales,  $A_{\text{exp}}(i) = -\log_{10}(\text{transmittance})$ , are offset to force coincidence at the peak maxima. Boron isotopomers of  $\text{BC}_5$ ,  $\text{BC}_6$  and  $\text{B}_2\text{C}_4$  are unresolved. The weaker of two bands of  $\text{B}_2\text{C}_5$  ( $I_{\text{theory}} = 1034 \text{ km mol}^{-1}$ , at  $1850 \text{ cm}^{-1}$ ) is shown here. Spectral resolution is limited to  $\sim 1 \text{ cm}^{-1}$  by matrix broadening. The lower detection limit is  $A_{\text{exp}}(i) \sim 0.001 \text{ cm}^{-1}$ .

and smallest for  $B_2C_{n-2}$ , which is consistent with a stratified matrix with a higher  $[C/B]$  ratio near the subliming surface. Apparently, boron evaporates more rapidly than carbon during the early stage of evaporation, resulting in boron-rich layers near the substrate.

The distribution of the  $n = 3$  clusters showed that their column densities are in the ratio  $\rho(C_3) : \rho(BC_2) : \rho(B_2C) : \rho(B_3) = 1.0 : 1.5 : 0.5 : < 0.05$ , where only the upper limit for  $\rho(B_3)$  may be determined because it was not observed. This is consistent with statistical formation of the trimers by condensation from well-mixed atoms in a matrix with  $[B/C] \sim 1/3$ , which would produce a  $1.0 : 1.0 : 0.33 : 0.05$  distribution, Eq. 1. Agreement between distributions implies trimers form by random condensation of well-mixed atoms, uninfluenced by the relative energies of the trimers, the energies of their precursors, or preferential kinetics pathways that could otherwise distort the statistics. Linear  $C_3$  and cyclic  $BC_2$ , disappeared entirely when the matrices were repeatedly annealed to temperatures between 25 K and 35 K, but cyclic  $B_2C$  was inert. Linear  $C_4$  and  $BC_3$  (BCCC) disappeared more slowly, and linear  $B_2C_2$  (BCCB) grew to  $\sim 95\%$  of its final value during the first annealing. Once formed,  $B_2C_2$ , like  $B_2C$ , was also inert to further reaction.

Figure 5 shows the absolute column densities of the analyzed clusters that were obtained by transformation of the Fig. 4 data with Beer's law and theoretical intensities shown in Fig. 1. The BC molecule was not observed, but its upper limit column density was established to be about equal to that of the  $B_2C_2$ . Thus, recombination of BC cannot be ruled out as the source of  $B_2C_2$ .

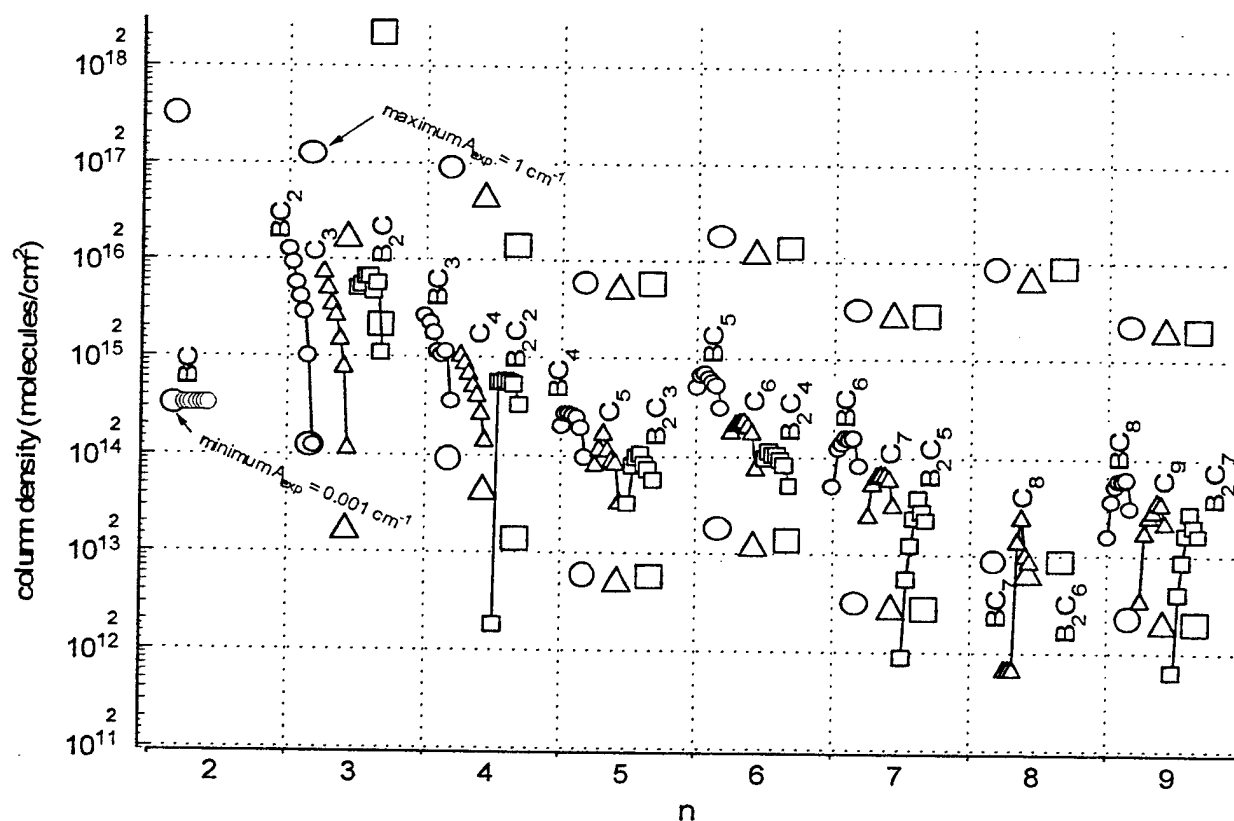


Figure 5. Distributions of  $B_nC_{n-J}$  clusters,  $J = 0, 1, 2$ ;  $n = 3 - 9$ . Circles, triangles and squares represent  $BC_{n-1}$ ,  $C_n$ , and  $BC_{n-2}$  clusters, respectively. Large symbols denote upper and lower limits of measurement, based on a nominal minimum measurable absorbance of  $0.0023 \text{ cm}^{-1}$ , and a maximum absorbance for linearity of Beer's law of  $2.3 \text{ cm}^{-1}$  (1% transmittance). Small symbols denote measured quantities in the initial matrix, and in six annealed matrices. Some of the larger clusters ( $n = 8, 10, 11$ ) have not been identified,  $BC_7$ ,  $B_2C_6$ ,  $BC_9$ ,  $B_2C_8$ ,  $BC_{10}$ ,  $B_2C_9$ .

In previous work [23, 25] on carbon matrices, annealing led to disappearance of atoms, dimers and trimers from the initial deposits. The identified products of recombination included cyclic  $C_6$  and cyclic  $C_8$ , and linear  $C_n$  molecules,  $4 < n < 13$ . After annealing to constant composition, the total measurable carbon was

found to be as much as twice the initial measurable carbon, indicating that about 50 % of the initially deposited carbon was isolated as atoms and dimers. The cyclic molecules, the dominant condensation products, amounted to as much as ~ 60% of total carbon in the fully annealed matrix.

In matrices containing boron, linear  $C_3$ , cyclic  $BC_2$ ,  $B_2C$ , and  $B_3$ , constituted about 80% of the total observable boron and carbon in the initially deposited matrix. Observation of approximately statistical distributions [Eq. 1] in clusters with  $n = 3, 4$ , and  $5$  in the initially deposited matrices implies that these smaller clusters form by random condensation of well-mixed atoms.  $C_3$  and  $BC_2$  disappeared entirely when the matrices were repeatedly annealed to temperatures between 25 K and 35 K, but cyclic  $B_2C$  was inert. Linear  $C_4$  and  $BC_3$  (BCCC) disappeared more slowly, and linear  $B_2C_2$  (BCCB) grew to ~ 95% of its final value during the first annealing. Once formed,  $B_2C_2$ , like  $B_2C$ , was inert to further reaction.

The sources of  $B_2C_2$  are from condensation of atom plus trimer ( $B + BC_2$  but not  $C + B_2C$ ) or dimer + dimer ( $BC + BC$  but not  $B_2 + C_2$ ). Although  $BC$  was not observed, the upper limit of  $\rho(BC)$  is larger than  $\rho(B_2C_2)$  so that  $BC$  cannot be ruled out as a source of  $B_2C_2$ . The growth of  $B_2C_2$  is conclusive evidence of the presence of  $BC$  and/or  $B$  in the originally deposited matrix in an amount at least as great as the growth of  $B_2C_2$ .

Linear  $C_5$ ,  $BC_4$  (BCCCC) and  $B_2C_3$  (BCCCB)] and larger linear clusters ( $B_JC_{n-J}$ ,  $5 < n < 11$ ,  $J = 0, 1, 2$ ), all grew upon annealing. The sources of  $B_2C_3$  are dimer + trimer ( $BC + BC_2$  but not  $B_2 + C_3$ ) and atom + tetramer ( $B + BC_3$  but not  $C + B_2C_2$ ). Since  $\rho(BC_2) \sim 5\rho(BC_3)$  in the initially deposited matrix, the  $BC + BC_2$  source is dominant. Growth of  $B_2C_3$  conclusively establishes the presence of  $BC$  in the matrix in an amount at least as great as the amount by which  $B_2C_3$  grows.

Growth of  $BC_4$  occurs primarily by  $BC + C_3$  rather than  $B + C_4$  or  $C + BC_3$  because  $\rho(C_3) \sim 10\rho(C_4)$  and  $\rho(C_3) \sim 2\rho(BC_3)$ . Growth of  $C_5$  occurs by  $C + C_4$  and  $C_2 + C_3$ , which establishes the presence of  $C$  and/or  $C_2$  in the original matrix in an amount at least as great as  $C_5$  growth.

## CONCLUSIONS

Disappearance of triangular  $BC_2$  requires breaking of one of its B-C bonds when one of its carbon atoms is attacked. The major reorganization of electronic energy involved in opening the ring appears to occur with little ( $< \sim 3$  kcal mol<sup>-1</sup>) or no energy barrier, which makes this small molecule a candidate for an interesting *ab-initio* study of unusual reactivity at low temperature. Annealing kinetics of disappearance of  $C_3$  and  $BC_2$ , and of appearance of  $B_2C$ ,  $C_4$ ,  $BC_3$ ,  $B_2C_2$ ,  $C_5$ ,  $BC_4$ , and  $B_2C_3$  unequivocally establishes the presence of atoms and dimers in the originally deposited matrix. About 80% or more of the initially deposited HEDM existed as atoms, dimers and trimers. Molecules with two boron atoms are immune from radical attack and condensation during annealing.

$B_2C_{n-2}$  clusters, once formed, were inert to further condensation upon annealing. Thus, energy loss by recombination during preparation of high energy density matrices (HEDM) is minimized in matrices with large B/C ratios. For example, when  $B/C \sim 2$ , any recombination that does occur during co-deposition would tend to produce  $B_2C$ , which is an inert molecule. In pure boron HEDM, the cyclic  $B_3$  molecule may be similarly inert, which would suggest that energy loss by recombination will also stop at a  $B_3$  "island of stability." The recent development of a novel high-flux boron atom source makes it possible to produce ~ 100 mg quantities of cryogenic solid HEDM containing 5 mole percent boron, primarily atoms.

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## REFERENCES

1. M. R. Berman, Editor, *Proceedings of the High Energy Density Matter (HEDM) Contractors' Conference* (8-10 June 1999, Cocoa Beach, Florida), published by Air Force Office of Scientific Research, Bolling AFB, DC 20332-8050, January 2000, and annual proceedings dating from 1987.
2. Simon Tam, Michel Macler, Michelle E. DeRose, and Mario E. Fajardo, "Electronic spectroscopy of B atoms and B<sub>2</sub> molecules isolated in para-H<sub>2</sub>, normal-D<sub>2</sub>, Ne, Ar, Kr, and Xe matrices," *J. Chem. Phys.* **113**, (2000) 9067.
3. Mark S. Gordon, Vassiliki-Alexandra Glezakou and David R. Yarkony, *J. Chem. Phys.* **108** (1998) 5657.
4. D. R. Yarkony, *J. Chem. Phys.* **109** (1998) 7047.
5. Muriel Wyss, Evgueni Riaplov, Anton Batalov, John P. Maier, Thomas Weber, Wilfried Meyer, and Pavel Rosmus, "Electronic absorption spectra of B3 and B3- in neon matrices," *J. Chem. Phys.* (2003, in press).
6. Vassiliki-Alexandra Glezakou, "The Interaction of Small Boron Clusters with Molecular Hydrogen," *Proceedings of the Molecular Dynamics & Theoretical Chemistry Contractors Review*, 18-20 May 2003 San Diego, California 2003, Mike Berman, editor, Air Force Office of Scientific Research Chemistry & Life Sciences Directorate.
7. Young K. Bae, "Stability of boron atoms in solid hydrogen," (in preparation).
8. Paul Nordine, "Advanced Rocket Propulsion Technologies, Boron Vapor Source for HEDM," SBIR Phase I Final Report, AFRL-PR-ED-TR-2003-0030, June 2003, Approved for Public Release, Distribution Unlimited.
9. J. D. Presilla-Márquez, C. W. Larson, P. G. Carrick, and C. M. L. Rittby, *J. Chem. Phys.* **105**, 3398 (1997).
10. J. D. Presilla-Márquez, P. G. Carrick, and C. W. Larson, *J. Chem. Phys.* **110**, 5702 (1999).
11. C. W. Larson and J. D. Presilla-Márquez, *J. Chem. Phys.* **111**, 1988 (1999).
12. G. Verhaegen, F. E. Stafford, and J. Drowart, *J. Chem. Phys.* **40**, 1622 (1964).
13. S. Becker, and H.-J. Dietze, *Intl. J. Mass Spectrometry and Ion Proc.* **82**, 287 (1988).
14. J. M. L. Martin, P. R. Taylor, J. T. Yustein, T. R. Burkholder, and L. Andrews, *J. Chem. Phys.* **99**, 12 (1993).
15. W. C. Easley and W. Weltner, Jr., *J. Chem. Phys.* **52**, 1489 (1970).
16. L. B. Knight, Jr., S. Cobranchi, E. Earl, and A. J. McKinley, *J. Chem. Phys.* **104**, 4927 (1996).
17. M. Wyss, M. Grutter, and J. P. Maier, *J. Phys. Chem. A* **102**, 9106 (1998).
18. J. M. L. Martin and P. R. Taylor, *J. Chem. Phys.* **100**, 9002 (1994).
19. S. Li, R. J. Van Zee, and W. Weltner, Jr., *Chem. Phys. Lett.* **262**, 298 (1996).
20. J. Niu, B. K. Rao and P. Jena, *J. Chem. Phys.* **107** 132 (1997).
21. I. Boustani, *Chem. Phys. Lett.* **233** 273 (1995), **240** 135 (1995).
22. A. Van Orden, and R. J. Saykally, *Chem. Rev.* **98**, 2313 (1998).
23. J. D. Presilla-Márquez, J. A. Sheehy, J. D. Mills, P. G. Carrick, and C. W. Larson, *Chem. Phys. Lett.* **274**, 439 (1997).
24. S. L. Wang, C. M. L. Rittby, and W. R. M. Graham, *J. Chem. Phys.* **107**, 6032 (1997).
25. J. D. Presilla-Márquez, J. Harper, J. A. Sheehy, P. G. Carrick, and C. W. Larson, *Chem. Phys. Lett.* **300**, 719 (1999).
26. S. L. Wang, C. M. L. Rittby, and W. R. M. Graham, *J. Chem. Phys.* **107**, 7025 (1997), **112**, 1457 (2000).
27. L. Lapinski and M. Vala, *Chem. Phys. Lett.* **300**, 195 (1999).
28. M. Wyss, M. Grutter, and J. P. Maier, *Chem. Phys. Lett.* **304**, 35 (1999).
29. M. Grutter, M. Wyss, E. Riaplov, and J. P. Maier, *J. Chem. Phys.* **111**, 7397 (1999).
30. A. K. Ott, G. A. Rechtsteiner, C. Felix, O. Hampe, M. F. Jarrold, R. P. Van Duyne, and K. Raghavachari, *J. Chem. Phys.* **109**, 9652 (1998).
31. C. M. L. Rittby, J. A. Sheehy, M. Vala, and M. Zerner (personal communications).
32. J. M. L. Martin, J. P. Francois, and R. Gijbels, *J. Chem. Phys.* **90**, 6469 (1989).
33. J. M. L. Martin, J. El-Yazal, and J. P. Francois, *Chem. Phys. Lett.* **242**, 570 (1995).
34. J. M. L. Martin and P. R. Taylor, *J. Chem. Phys.* **100**, 9002 (1994).